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# SPECIFICATION

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Inventor: WITOLD TITOW

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## COMPLETE SPECIFICATION

### Production of Particulate Inks

GREAT BRITAIN  
GROUP 146  
CLASS 104  
RECORDED

We, MOLINS MACHINE COMPANY LIMITED, a British Company of 2 Evelyn Street, Deptford, London, S.E.8., do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to cellular particulate inks consisting of solids material.

Particulate inks are used in electrostatic printing, magnetic printing, in certain copying processes, and in dry powder printing applications; certain types of these inks are sometimes referred to as "toners".

In many of the above mentioned processes the optimum particle size for the ink is from 5 to 30 microns (for some purposes an even narrower range of from 5 to 15 microns is preferred) and it is often not practicable with the aid of image-forming means of the particular process involved, to deposit a layer of ink which is no thicker than that required to produce a good print. For example, in electrostatic printing processes it is frequently necessary to deposit layers of ink far thicker than would normally be required to produce a good copy. The thickness of the layer actually deposited may be associated with the degree of insulation required to counteract or neutralise the charge on the substrate material to the point where further deposition of ink particles is prevented. Obviously the deposition of unnecessarily large quantities of ink particles in relation to the quantity necessary for producing a good copy is very wasteful of materials.

The present invention provides particulate inks in which the particles have the required size range but contain a proportion of voids so that the actual solids content of an ink layer ostensibly thicker than neces-

sary is not substantially greater than the quantity required to produce a good print. 45

For example, a layer of particulate ink containing 90% of voids will have only 10% of the solids content of a similar layer of solid particulate ink, although the cellular particles will have the required optimum size characteristics consistent with the requirements of the particular ink transfer process and equipment being used and will fulfil the requirements of lack of background colouration on deposition.

Accordingly the present invention provides a particulate ink in which the ink particles consist of solids material and are cellular.

The cellular particulate inks of the present invention have the same chemical composition as conventional particulate inks, i.e., in general they will consist of a resinous binder, a colourant and possibly finely divided fillers, as well as other conventional additives in small proportions. The particulate inks of the present invention will, however, contain voids in their particle structure which distinguishes them from conventional solid ink particles; these voids may be such that the ink particles are in the form of porous granules or of hollow shells, in which case each particle is a single cell.

A further advantage of the cellular particulate inks provided by the present invention is that they show considerable advantages over conventional solid particulate inks at the print fixing stage. It is usual in printing with particulate inks to "fix" the printed image after deposition by the application of heat or vapours of a solvent, or both. With these fixing methods, in particular with solvent vapour fixing, the very much greater specific surface offered by the cellular particulate inks provided by the present invention makes for

more rapid print fixing, especially if the cells of the particulate ink are intercommunicating.

The percentage of voids in the particulate inks according to the invention will be chosen in accordance with the ink transfer process and equipment in which they are to be used. Ideally this percentage will be that which leads to the most economic use of ink material by providing that a particulate ink layer of the thickness required by the ink transfer process contains no more ink material solids than are required to produce a good print.

15 The cellular particulate inks provided by the present invention can be produced by a number of methods conventional for the production of expanded solids. One such method is the inclusion in the ink composition during production of a solid material soluble in a selected solvent, followed by leaching out this material with the solvent after the formation of the particles. Another method is the incorporation in the ink 20 composition of a blowing agent which is activated at the particle formation stage or later, after the particles have been formed.

A suitable process employing a blowing agent comprises forming a solution of the necessary components, that is the resinous binder, the colourant and the blowing agent in a solvent, finely dispersing the solution in a liquid medium which is a non-solvent for the resinous binder, heating the dispersion to a temperature below the boiling point of the non-solvent liquid to volatilise the solvent of the solution, to soften the resinous binder and to activate the blowing agent, and separating from the non-solvent liquid the cellular particles formed. In carrying out this process, the non-solvent liquid used must, of course, have a higher boiling point than the solvent of the initial solution.

In another process, a solution containing the resinous binder, the colourant and the blowing agent is spray dried in air or another gaseous medium, the solvent being volatilised, the resinous binder being softened and the blowing agent being activated during the spray drying operation.

The quantity of blowing agent used in these processes will depend upon the nature of the components of the ink material and upon the required voids content and cell structure of the ink particles but, in general, will be within the range of from 0.01% up to several per cent.

The melting or softening point of the resinous binder will determine the temperature of the heating stage during which expansion of the particles takes place and the blowing agent will be so chosen as to be activated at the relevant temperature. For example, an ink in accordance with the present invention can be produced from a solu-

tion of a polyamide (Versamid 940) dissolved in chloroform to form a solution of 5 to 20% solids content. Waxoline Red is added to the solution in an amount of 1% based on the total solids content. A blowing agent is added to the composition. Such a composition can then be spray dried in a conventional spray drier in air, the air stream temperature being from 100 to 120°C to ensure the softening of the polyamide resin while blowing proceeds. Under these conditions, and with this composition, the blowing agent used should be such as will be activated at a temperature of from 60 to 80°C; a blowing agent suitable for use with the composition described above is the morpholine salt of nitro-urea.

The above general example illustrates the basic features of one variant of the process used to produce an ink according to the present invention with the use of a blowing agent, but obviously modifications of this process are possible. For example, in some cases the solvent used to dissolve the resinous binder may itself act as the blowing agent by appropriate variation of the temperature and/or pressure of the medium into which the solution is introduced during the blowing stage. In addition it is also possible to carry out the cellular particle formation in two stages, for example by removing the solvent first, collecting the particles and blowing them in a separate step, for example, by dispersing them in a liquid medium which is a non-solvent for the resinous binder or in a gaseous medium and heating them while so dispersed to a temperature at which the blowing agent is activated.

The invention will be more fully understood from the following Examples which are given by way of illustration only.

#### Example 1

A solution of:

50g "Versamid" 940 (trade mark) 110  
450g Chloroform  
0.5g "Waxoline Red O.S." (trade mark)

was prepared by dissolving the solids in the solvent on the rollers in the cold, and to the resulting solution was added 390g of methanol and 5 ml. of a 10% solution of the morpholine salt of nitro-urea in methanol.

The mixture was then spray dried in a laboratory spray drier ("NIRO" Mobile Minor model—Niro Atomiser A.S.) using an inlet temperature of 125°C and an outlet temperature of 88°C. This produced a particulate product having a particle size from 10 to 20 microns with a density of 0.15g/cc (density of Versamid 940:0.98g/cc).

#### Example 2

10g of titanium dioxide filler ("Tiona P" —trade mark—Laporte Chemicals) was dis-

persed thoroughly in a solution of 25g "Piccolastic" A75 (trade mark; a polystyrene blend) in 225g methylene chloride with a Silverson Stirrer. To the resultant suspension there was added, with stirring:

50g water

1g non-ionic surfactant "Lissapol" N (trade mark)—described by I.C.I. as nonyl phenol ethoxylate.

10 The mixture was then introduced into a laboratory spray dryer with a continuous agitation and spray dried ("Niro" Mobile Minor atomiser) using an inlet temperature of over 100°C and an outlet temperature of 15 over 40°C.

15 The particle size range of the product was 10—50 microns and its density was lower than that of the "Piccolastic". Indications of cellular structure were obtained on examination under a microscope.

*Example 3*

A mixture was prepared of the following ingredients:—

13g "Piccolastic" A75

25 7.5g Pale solid Coumarone resin

3.5g Pale liquid Coumarone resin

2g "Tiona" P

1g "Waxoline" Red O.S.

200g Chloroform

30 30 ml. of the mixture was dispersed with a Moritz stirrer in 250 ml. glycerol at room temperature. The resultant dispersion was then maintained at 50° — 55°C for 2 hours with continuous stirring, after which it was

35 poured into 2 litres of water and filtered. Large, hollow "egg-shell" particles were produced having an average particle size of 200 microns.

*Example 4*

40 A solution was prepared of the following ingredients:—

25g "Versamid" 940

225g Toluene/isopropyl alcohol (1:1)

3.5g E.B. Spirit Black

45 The solution was stirred with a Silverson stirrer and a solution of 10g dicyandiamide in 120g acetone/water (1:1) was added and the resulting dispersion spray-dried ("Niro" Mobile Minor spray dryer) using an inlet temperature of 120°C and an outlet temperature of 75°C, to produce a particulate product having a particle size of 3 — 10 microns.

50 10g of this product was soaked in 100 ml. cold distilled water for 48 hours and then filtered off and dried under vacuum at 40°C for 16 hours. A weight loss of 40% had occurred during drying, the particle size remaining constant. The particles obtained were cellular.

**WHAT WE CLAIM IS:—**

1. A particulate ink in which the ink particles consist of solids material and are cellular.

65 2. A particulate ink in which the ink

particles consist of solids material and are composed of a resinous binder and a colourant, each ink particle containing one or more voids.

3. A particulate ink according to claim 2 which also comprises a finely divided filler.

4. A particulate ink according to any of claims 1 to 3, in which substantially all the particles have a particle size of from 5 to 30 microns.

5. A particulate ink according to any of claims 1 to 3, in which substantially all the particles have a particle size of from 5 to 15 microns.

6. A process for the preparation of a particulate ink consisting of solids material, which comprises forming particles from a composition comprising a resinous binder, a colourant and a soluble solid material and leaching the soluble material out of the particles with a solvent for the soluble material in order to create voids in the particles.

7. A process for the preparation of a particulate ink consisting of solids material, which comprises forming particles from a composition comprising a resinous binder, a colourant and a blowing agent and activating the blowing agent at a temperature at which the resinous binder is softened in order to create voids in the particles.

8. A process according to claim 7, in which a solution of the resinous binder, the colourant and the blowing agent in a solvent is finely dispersed in a liquid medium which is a non-solvent for the resinous binder, the dispersion is heated to a temperature below the boiling point of the non-solvent liquid to volatilise the solvent of the solution, to soften the resinous binder and to activate the blowing agent, and the cellular particles formed are separated from the non-solvent liquid.

9. A modification of the process according to claim 8, in which the dispersion is heated to a first temperature to volatilise the solvent and is then heated to a higher temperature to activate the blowing agent.

10. A modification of the process according to claim 8, in which the dispersion is heated to volatilise the solvent, the blowing agent being such that it is not activated at the temperature at which volatilisation is effected, the particles are separated from the non-solvent liquid and are dispersed in another non-solvent liquid or in a gaseous medium and while so dispersed are heated to a temperature at which the blowing agent is activated, and the void-containing particles obtained are then separated from the liquid or gaseous dispersion medium.

11. A process according to claim 7, in which the particles are formed by spray drying a solution of the resinous binder, the colourant and the blowing agent in a solvent,

the blowing agent being such that it is activated at the temperature at which spray drying is effected.

12. A process according to claim 11, in which the resinous binder is a low-melting polyamide, the blowing agent is one that is activated at a temperature of from 60° to 80°C, and spray drying is carried out at a temperature of from 100° to 120°C.

10 13. A cellular particulate ink substan-

tially as herein described in any of the Examples.

14. A process for the preparation of a particulate ink substantially as herein described in any of the Examples

A. A. THORNTON & CO.  
Chartered Patent Agents,  
Northumberland House,  
303/306 High Holborn,  
London, W.C.1.

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